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Supporting Information

Tailoring Natural Layered β-phase Antimony into Few-layer Antimonene for Li Storage with High-rate Capabilities

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Fabrication of few-layer antimonene: All the chemicals were purchased from Aladdin and used without further purification. Few-layer antimonene were prepared by liquid exfoliation in ultrasonic bath which is made by Dongguan Mojie Ultrasonic Equipment Co. LTD. We tested a series of experimental conditions to obtain the optimized parameters. First, 200 mg commercial antimony powders were added into 80 mL NMP. Then the mixture was sonicated for five hours at the power of 200 W. In order to avoid oxidation, 99.9 % Ar was bubbled into the mixture during the exfoliation. The resultant dispersion was centrifuged for 20 minutes at speed of 3000 rpm. Finally, the supernatant containing antimonene was decanted gently.

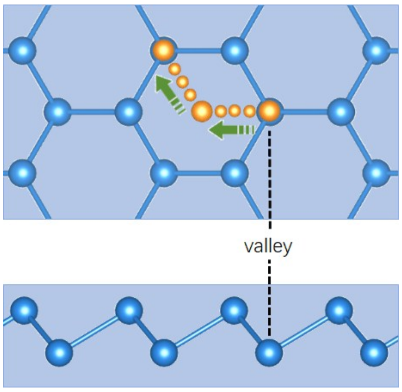
Fabrication of few-layer Sb NPs: Sb NPs were prepared by ultrasonic cell grinder which is made by Shenzhen Prestige Ultrasonic Equipment Co. LTD. The prepared antimonene colloid was further sonicated by the probe for a total of 1 hour with ice bath at the power of 1 kW. High purity Ar was also bubbled into the mixture during the exfoliation.

Characterization of few-layer antimonene and Sb NPs: XRD patterns were recorded on a Bruker D8 multipurpose XRD system. SEM images were obtained by FEI Quanta 250FEG. AFM measurements were carried on a Bruker Multimode 8 AFM system. Raman spectrum obtained by Aramis made by HORIBA JOBIN YVON at 532 nm. The antimonene dispersion was dropped onto a micro Cu grid, and toluene was allowed to evaporate at room temperature. TEM and HRTEM images were taken on a FEI Titan 80-300 Cs-corrected electron microscopy. X-ray photoelectron spectroscopy was conducted on AES-XPS instrument (AXIS-ULTRA DLD-600W).

Computational Methods

All the calculations are performed using the DMol3 code from Materials Studio package. All the structures are optimized by Perdew-Burke-Ernzerhof (PBE) including van der Waals corrections [S1]. In addition, we use the double numerical plus polarization (DNP) to expand electronic wave function. For Sb monolayer, a vacuum space of 18 Å is applied to avoid spurious interactions. The transition state search is using the complete LST/QST method [S2].

To calculate possible diffusion barriers, we first investigated the stable adsorption site on 2D anitmonene. It was found the most stable adsorption site is the valley site which is interacted with more neighboring Sb atoms. Transition state (TS) search based on complete LST/QST method was presented to find the energy minimum path between two equivalent adsorption sites that is the most favorable.



Electrode fabrication and measurements: The electrochemical performance of both antimonene and Sb NPs were evaluated using coin-like 2025 cells assembled in an argon-filled glove box. To prepare the electrodes, the active materials, carbon black, and carboxymethyl cellulose (CMC) were mixed at a ratio of 65:20:15 and water was added dropwise to form a slurry. The slurry was put on a copper foil and vacuum-dried at 120 °C for 24 h. The mass loading of the active materials in the electrode was about 1.0 mg cm^{-2}. The Li metal acted as the counter electrode and glass fiber (Whatman) served as the separator. The electrolyte was 1 M $LiPF_6$ (99.99%, Sigma-Aldrich) in a 1:1 vol/vol mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Cyclic voltammetry (CV) was performed on an electrochemical workstation (CHI 660E, Shanghai, China) at a scanning rate of 0.1 mV s^{-1} between 0.01 and 1.5 V versus Li^+/Li. Electrochemical impedance spectroscopy (EIS) was conducted on the same instrument at frequencies between 100 kHz and 0.01 Hz with an amplitude of 5 mV. The galvanostatic charging-discharging (GCD) tests were carried out on the Xinwei instrument (Shenzhen, China) and the cutoff voltage was varied from 0.01 to 1.5 V versus Li^+/Li. The specific capacities were calculated on the basis of the mass of the active FLA (1 C = 660 mA g^{-1}) and all the electrochemical tests were performed at room temperature.

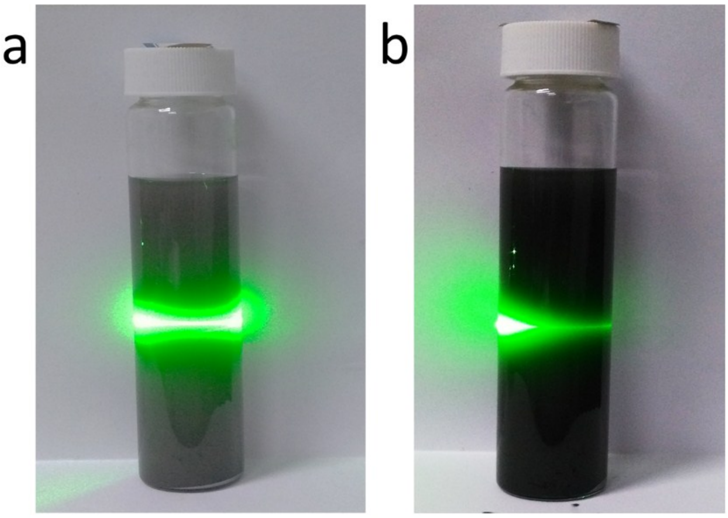


Figure S1. Photographs of antimonene colloid (a) and Sb QDs colloid (b) with Tyndall effect.

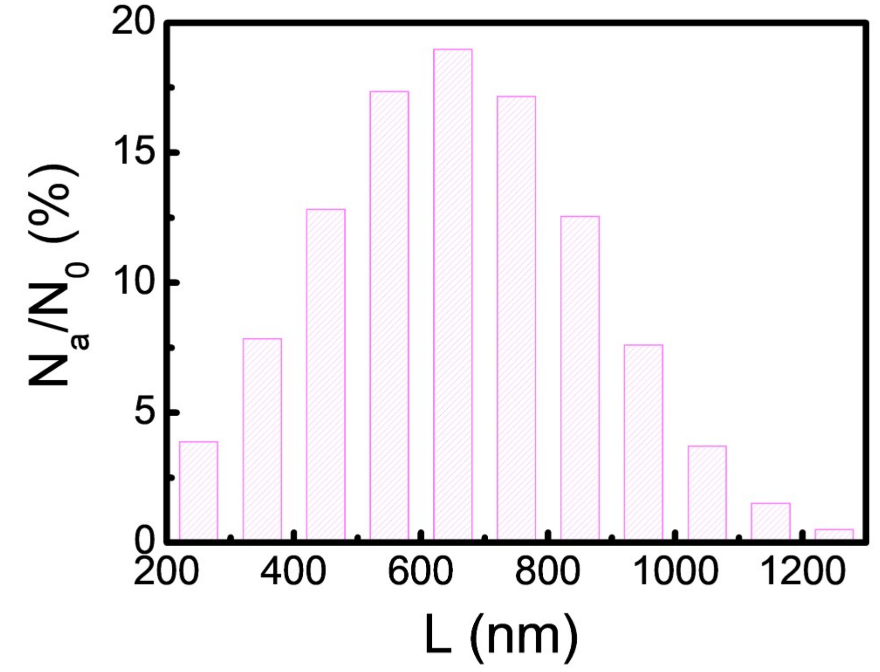


Figure S2. The statistical diagram of nanosheets lateral size on 100 flakes.

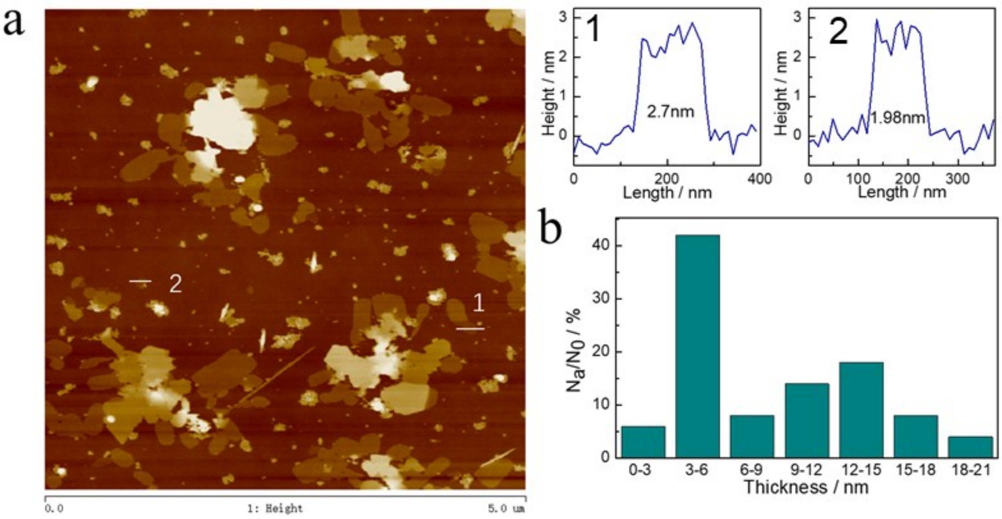


Figure S3. (a) AFM image of deposited few layer antimonene on SiO_2 /Si substrate and the height analysis of typical samples. (b) Statistical histogram of the thickness on 100 nanosheets.

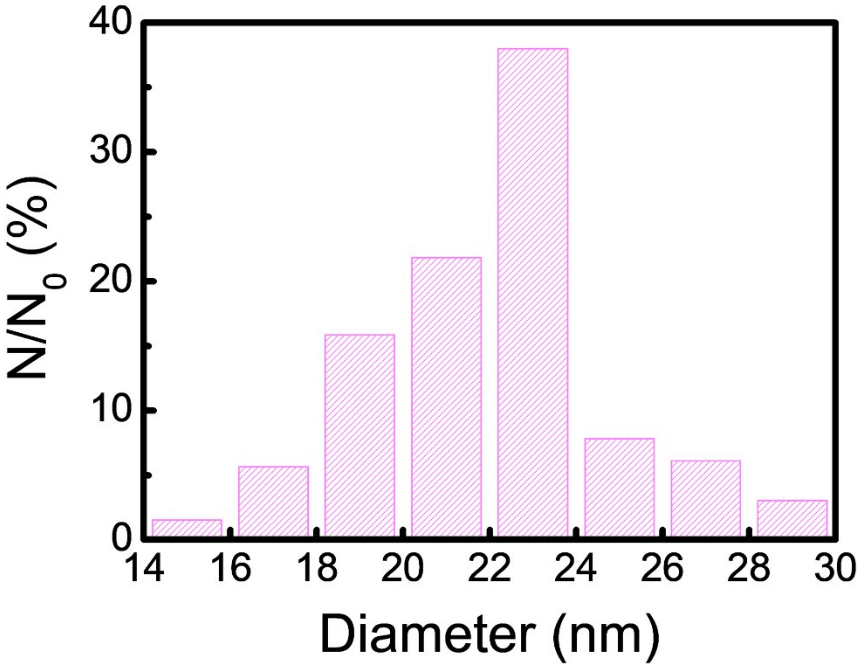


Figure S4. The statistical diagram of Sb QDs lateral size on 100 flakes.

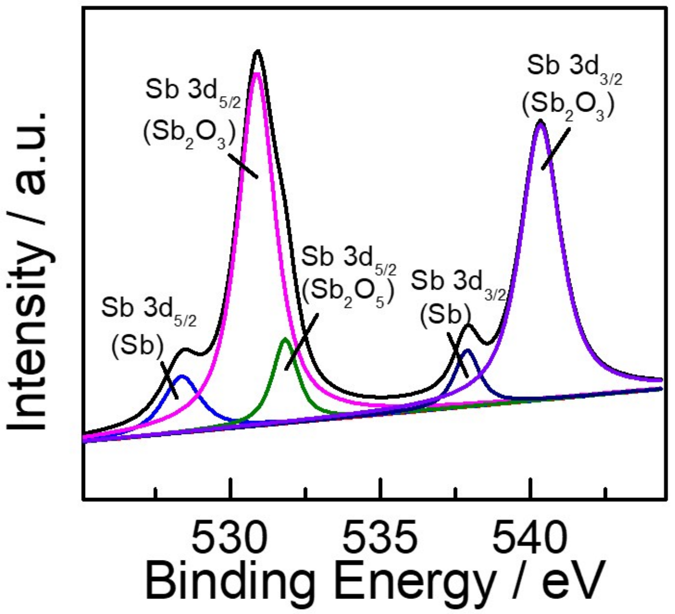


Figure S5. High-resolution Sb 3d XPS spectrum of bulk antimony.

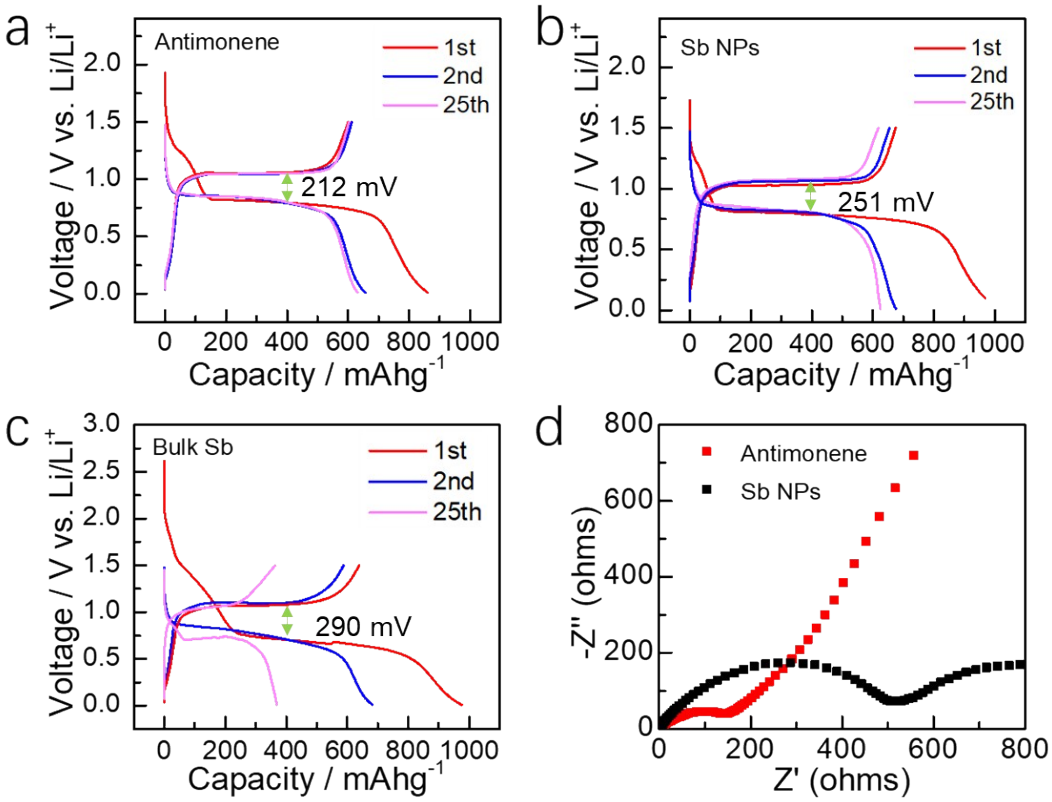


Figure S6. The charge-discharge profiles of antimonene (a), Sb nanoparticle (b) and bulk Sb (c), respectively. (d) The electrochemical impedance spectroscopy (EIS) of both antimonene and Sb NPs.

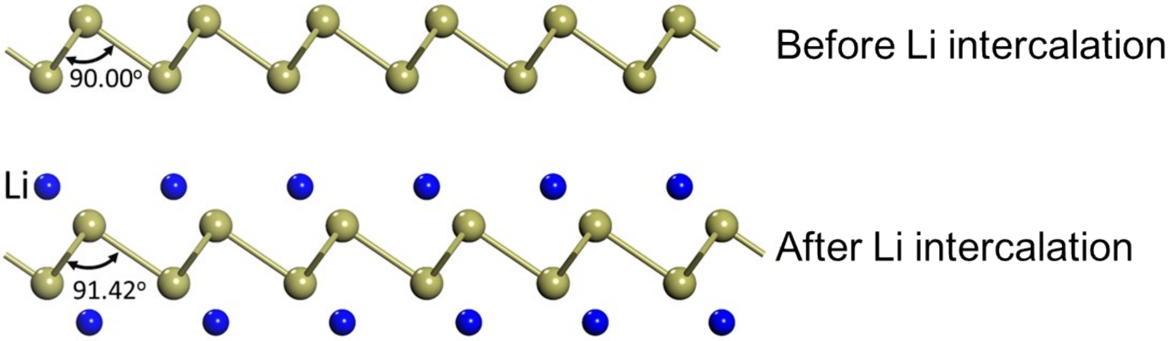
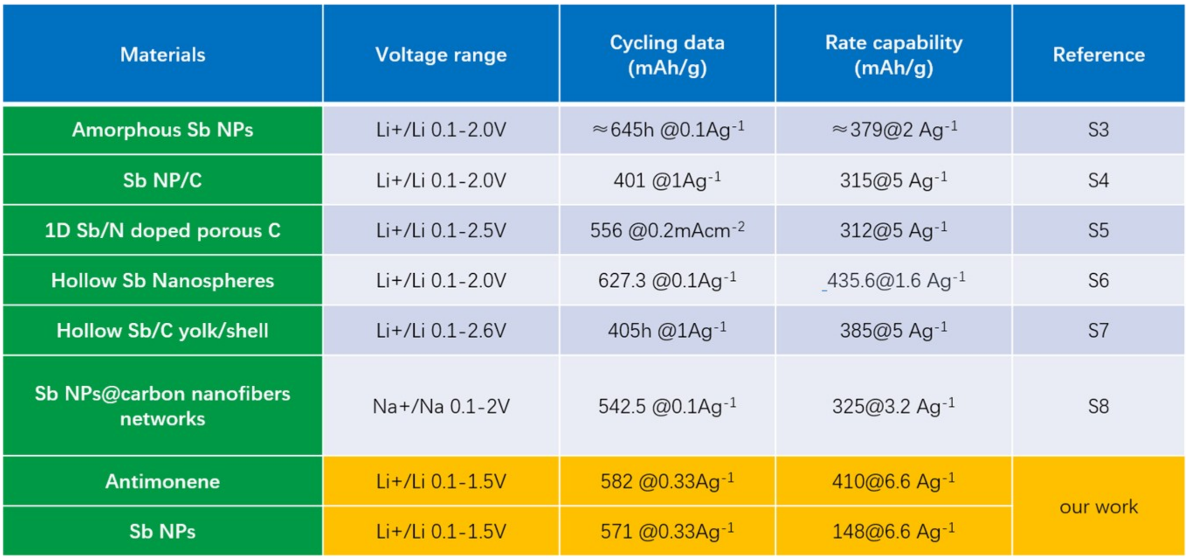


Figure S7. The adjacent side angle changes of antimonene after Li intercalation (blue ball: Li^+)

Table S1. Comparison of the Li-storage performance of nanostructured Sb material.



Materials	Voltage range	Cycling data (mAh/g)	Rate capability (mAh/g)	Reference
Amorphous Sb NPs	Li+/Li 0.1-2.0V	$\approx$645h @0.1Ag^{-1}	$\approx$379@2 Ag^{-1}	S3
Sb NP/C	Li+/Li 0.1-2.0V	401 @1Ag^{-1}	315@5 Ag^{-1}	S4
1D Sb/N doped porous C	Li+/Li 0.1-2.5V	556 @0.2mAcm^{-2}	312@5 Ag^{-1}	S5
Hollow Sb Nanospheres	Li+/Li 0.1-2.0V	627.3 @0.1Ag^{-1}	435.6@1.6 Ag^{-1}	S6
Hollow Sb/C yolk/shell	Li+/Li 0.1-2.6V	405h @1Ag^{-1}	385@5 Ag^{-1}	S7
Sb NPs@carbon nanofibers networks	Na+/Na 0.1-2V	542.5 @0.1Ag^{-1}	325@3.2 Ag^{-1}	S8
Antimonene	Li+/Li 0.1-1.5V	582 @0.33Ag^{-1}	410@6.6 Ag^{-1}	our work
Sb NPs	Li+/Li 0.1-1.5V	571 @0.33Ag^{-1}	148@6.6 Ag^{-1}	

Reference

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